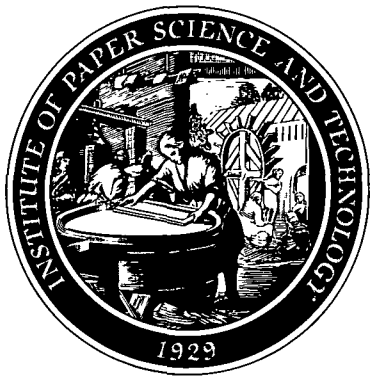

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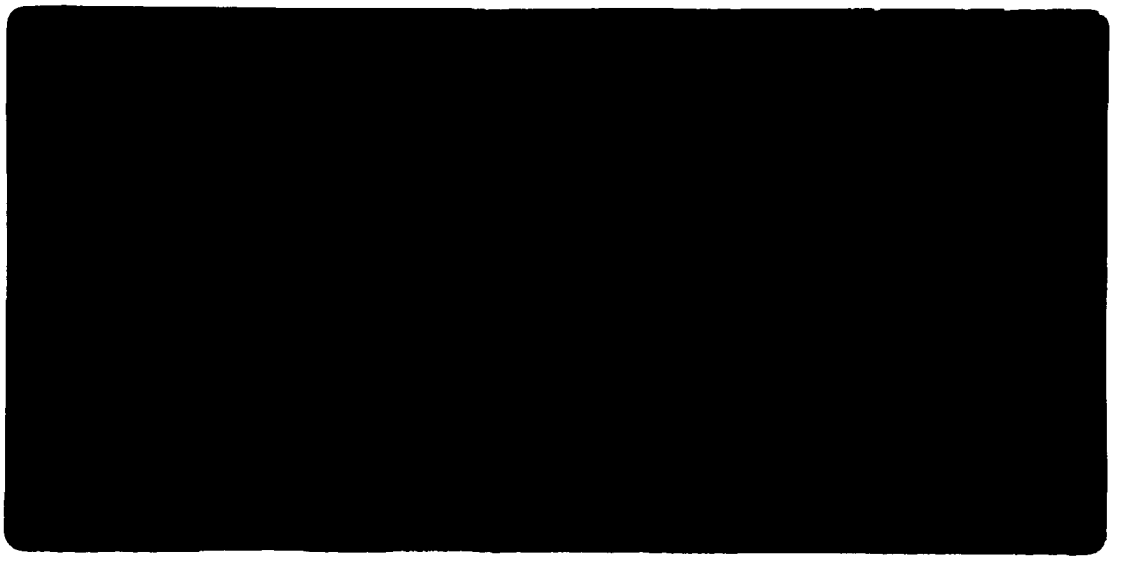

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LIPOPHILICITY OF A SYNTHETIC BLEACHED KRAFT EFFLUENT

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Lipophilicity of a Synthetic Bleached Kraft Effluent

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Abstract

Kraft pulp was bleached with chlorine tagged with ^{36}Cl. The octanol:water partition coefficient (K_{ow}) of the collective labeled organic products in the spent solution was 0.03, which is identical to the K_{ow} of water. This unusually low value is believed to arise from a low activity coefficient in water combined with a corresponding high value in octanol. It follows that chlorinated bleach mill effluents will tend to move with the water column. Biological effects are likely to be associated with the small proportion of lipophilic components in the effluent which should progressively partition out of the water column with flow. Hence, a direct correlation between total organochlorine concentration and biological effect is not expected. Chlorinated materials formed in the pulp matrix did not leach significantly into octanol.

Introduction

An average of 5 kg. of chlorinated organic material results from each metric ton of Kraft pulp bleached by conventional chlorine-based sequences (1,2). Bleached Kraft mill effluent (BKME) contains high-profile contaminants such as chlorophenols as well as numerous high molecular weight compounds that are largely uncharacterized (1,3). Although the lipophilicity of many BKME components is known (4), a composite K_{ow} value that applies to all the chlorinated compounds in BKME is not available. In this study, we determine this K_{ow} in order to model the environmental transport and distribution of the chlorinated component of BKME.

Experimental

An oxygen-delignified and a non-oxygen delignified Southern pine Kraft pulp of kappa number 14.7 and 26.6, respectively, were used. The pulps were hand-washed and brought to 24% consistency (solids level in water) by vacuum filtration with recycling of filtrate. Radioactive chloride ($^{36}Cl^-$) as HCl (9.48 mCi/g) was purchased from du Pont.

Scintillation counting was done on a Beckman 3704 instrument. A counting efficiency of 88% was determined for ^{36}Cl.

Preparation of Radioactive Chlorine

Molecular chlorine is in equilibrium with ionic species through the processes

$$Cl_2 + H_2O = HOCl + HCl$$
$$Cl_2 + Cl^- = Cl_3^-$$

Thus, if $^{36}Cl^-$ is added to an aqueous chlorine solution, the isotope should rapidly equilibrate to give labeled chlorine. In order to verify this, a chlorine solution containing $^{36}Cl^-$ was added to an aqueous solution of phenol at pH 11. The chlorination of phenol is rapid and forms mostly chlorophenol when the phenol is held in excess. If radioactive chlorine is formed as expected, then approximately half the isotope should be converted to chlorophenol.

The solution was acidified with concentrated nitric acid after a 30 minute reaction period, extracted with toluene, and counted for radioactivity. If all the chlorinated products from phenol extracted into toluene, then half of the initial radioactivity would transfer to the toluene phase with the other half remaining in water as inorganic chloride. We found the organic:aqueous phase distribution of radioactivity to be 40:60. Clearly, the added $^{36}Cl^-$ is cycled into labeled molecular chlorine.

Pulp:water Distribution of Chloride Ion

One of our objectives was to determine the fraction of the initial chlorine applied that terminates in products inextricably bound to pulp. In order to assign all the counts in pulp to organochlorine products, it was necessary to verify that chloride ion has a very low affinity for pulp. A Kraft loblolly pine pulp suspension at 3% consistency (solids level) was spiked with $^{36}Cl^-$, and the mixture was equilibrated for 1 hour at 60°C. The mixture was then centrifuged, and 97.0±0.1% of the activity was recovered in the solution phase,

confirming the preference of $^{36}Cl^-$ for the aqueous phase.

Bleaching Experiments

Bleaching was conducted in a 40 mL glass vessel sealed with a paraffin-coated stopper. Pulp (0.5 g. on an oven-dried basis at 3% consistency) and the bleaching agent were sequentially added to the vessel, and the mixture was mechanically stirred at 50°C for 1 hour. During Cl_2/ClO_2 bleaching, the ClO_2 was added 1 minute prior to Cl_2 addition. The mixture was vacuum-filtered, and the solids resuspended to 5% consistency for the caustic extraction stage. NaOH was added to the pulp suspension and the mixture stirred for 1 hour at 70°C. The suspension was again vacuum-filtered, and the pulp washed with water.

The chlorination/extraction conditions were as follows.

(a) 100% Cl_2; 3.4% active chlorine applied; extraction stage: 40% and 7% NaOH by weight;

(b) 76% Cl_2 and 23% ClO_2; 3.9% active chlorine applied; extraction stage: 40% and 7% NaOH by weight;

(c) 100% Cl_2; 4.3% active chlorine applied; extraction stage: 7% NaOH by weight.

The percent active chlorine applied is the weight of the Cl_2 and ClO_2 (in Cl_2 equivalents) applied per 100 g. of oven-dried pulp.

The component of the filtrate associated with chlorinated organics was determined from the counts as follows. In a typical experiment, the filtrate contained 17,341 dpm/mL. The activity in the initial ^{36}Cl stock solution (before its addition to aqueous chlorine) was 2.164E10 dpm/g. Thus, the activity in the filtrate corresponds to 0.801 ppm of ^{36}Cl material. The Cl_2 mass in the bleaching solution was 17.17 mg. as determined by iodometric titration. A count of the solution showed its ^{36}Cl content to be 0.0163 mg. Thus, ^{36}Cl constituted 0.095% of the total chlorine mass.

Chloride ion was determined to be 395 ppm in the filtrate by ion chromatography.

Of this, 0.095% or 0.374 ppm was $^{36}Cl^-$. Since the filtrate contained 0.801 ppm of ^{36}Cl as discussed above, the difference (0.427 ppm) of ^{36}Cl must be associated with tagged chlorinated organic products. Thus, the chlorine fraction of the total labeled and unlabeled chlorinated organic products (Cl_{org}) is 0.427/0.00095 or 450 ppm.

Pulp was separated from the mixture by vacuum filtration. The filtrate was recycled through the pulp mat in order to simulate actual mill operating conditions and to recapture fines. The extracted pulp was washed with 5 mL of 70°C distilled water prior to collection and storage.

Octanol Extractions

The filtrates were extracted with an equal volume (2 mL: 2 mL) of octanol. Pulp (0.5 g.) at 32% consistency was extracted with 2 mL of octanol. Octanol extractions were done by shaking vigorously for 10 minutes and allowing the phases to separate over 48 hours. The octanol:water partitioning of chloride ion was expected to be very small, and to confirm this, $^{36}Cl^-$ (1420 dpm) as HCl was added to 1 mL of water and extracted with 1 mL of octanol. No counts were detected in the octanol phase. This result is consistent with the reported value of 0.001 (5) for the K_{ow} of NaCl.

The tagged material in the filtrate represents both chloride ion and chlorinated organic material. In order to obtain the octanol:water distribution coefficient (K_{ow}) of the chlorinated organic compounds, the activity in the octanol and water phases was measured by scintillation counting. The activity in the octanol phase was attributed in its entirety to chlorinated organics. That in the water phase was corrected for $^{36}Cl^-$ activity determined through ion chromatography.

Results and Discussion

The distribution of effluent components was determined with radiolabeled material prepared by bleaching pulp with $^{36}Cl_2$. Use of ^{36}Cl allows the direct and unambiguous quantitation of organochlorine in water, octanol, and pulp. The activity in the filtrates

and pulps determined at various stages of the bleaching sequence is presented in Table 1. Recoveries range between 69% and 82%, and the loss probably reflects the escape of chlorine gas and volatile products. As expected, the bulk (80%-84%) of the recovered activity was found in the C-stage filtrate. No radioactivity was released when the pulp fraction in Table 1 was extracted with octanol, confirming that most of the chlorinated material in pulp is inextricably bound and is presumably not bioavailable.

The C-stage pulp used in the first entry of Table 1 was extracted as a function of NaOH concentration, and the activity recovered is listed in Table 2. No real improvement in extraction efficiency occurs beyond a charge of 7% NaOH. It would seem that the lower levels of caustic remove Cl^- and low molecular weight materials, and the larger compounds dissolve at higher caustic strength.

The Table 1 data suggest that most of the activity remaining in the pulp after the C-stage can be removed in the E-stage. The C-stage data in Table 1 are further expanded into Cl^- and Cl_{org} fractions in Table 3. No real differences in the $[Cl^-]$:$[Cl_{org}]$ ratio can be interpreted owing to the high uncertainty. This value is a measure of the ratio of oxidation to substitution between lignin and the oxidant. The K_{ow} values in Table 3 are similar for all the conditions examined, and average out to 0.03. This remarkably low value is the same as that for water (6). Although organic compounds that are as lipophobic as water are relatively uncommon, there is ample available precedent (7). For example, the K_{ow} for sucrose is $K_{ow}=0.0002$; that for glycerol is 0.02. Activity coefficients for highly polar compounds in the octanol phase (γ_{oct}) are much higher than those for the water phase (γ_w). Also, activity coefficients in octanol tend to increase with molecular size (6,8,9). It has recently been shown (10) that the molecular weight of chlorinated material in BKME averages to 200-550. Highly polar materials in this weight fraction should give rise to a low γ_w and a high γ_{oct}, which translates to a low K_{ow} value.

It is known that about 0.1% of BKME components have $K_{ow}>3$ (3). These are the

compounds of principal environmental concern, and their mobility will be attenuated by sorption to soil and sediment. Thus, the environmentally important components will be less mobile than the others, and a correlation between environmental effects and total chlorine load is not expected. These conclusions are consistent with the work of Hodson et al. (11) who demonstrated differential mobility for a number of effluent components. The majority of the components, however, will tend to move with the water column; their low K_{OW} provides a basis for recent observations (11,12) of their presence 100 km. downstream of the mill.

In summary, the average lipophilicity of BKME is about the same as that of water, and the transport of these materials should parallel that of water. The bioconcentration potential of these compounds are minimal, and their primary removal mechanism from the water column should be through degradation. It is strongly emphasized that these conclusions apply to BKME as a family, and should not be applied to a subset of components contained therein.

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Table 1: Distribution of ^{36}Cl in Pulp and Effluents

pulp type[b]	percent Cl applied	percent NaOH applied	recovery[c]	percent distribution of recovered ^{36}Cl[a]			
				C	E	E_{pw}	pulp
A	3.4	40	82	80	13	2	5
		7	82	83	14	1	3
A	3.9[d]	40	77	82	15	1	1
		7	69	83	13	2	3
A	4.3	7	79	82	13	2	3
B	3.4	7	82	85	13	1	1

[a]C:chlorination effluent; E:extraction effluent; E_{pw}: pulp wash following extraction; [b]A: oxygen delignified; B: non-oxygen delignified; [c]of total ^{36}Cl applied; [d]23% ClO_2 substitution.

Table 2: E stage extraction efficiency vs. applied alkali

percent caustic applied	percent activity recovered
0	5
1	6
2	7
4	8
7	14
40	15

Table 3: K_{ow} values for C-Stage Effluent

pulp type[a]	percent Cl applied	$[Cl^-]$ ppm	$[Cl_{org}]$ ppm	K_{ow}	n
A	3.4	468±48	363±58	0.027±0.08	3
A	3.9[b]	393±15	278±126	0.046±0.026	3
A	4.3	692±170	264±60	0.029±0.013	3
B	3.4	977	385	0.029	1

[a]A: oxygen delignified; B: non-oxygen delignified;
[b]23% ClO_2 substitution.